

Microscopic estimation of the deformation potential in a structural model glass

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Starting from a microscopic Hamiltonian we analyze the coupling between tunneling systems (TS's) and phonons in a structural model glass, chosen to describe NiP. We estimate the TS-phonon coupling constants, i.e., the longitudinal and transverse deformation potentials γ_l and γ_t . They are proportional to the spatial distance between the two energy minima. This dependence translates into an energy dependence of the deformation potential, which is relevant for the temperature dependence of the low-temperature thermal conductivity. On the basis of TS's in NiP found via a computer search in our previous work we obtain the values $\gamma_l=0.38$ eV and $\gamma_l^2/\gamma_t^2 \approx 2.35$. We analyze the influence of the structure of typical TS's on the deformation potential. Together with the density of tunneling systems determined in a previous paper the interaction between tunneling systems can be calculated. In contrast to recent proposals, the weak-coupling picture and hence the validity of the standard tunneling model is confirmed.

I. INTRODUCTION

The properties of glasses at very low temperatures ($T < 1$ K) can be nicely explained in the framework of the standard tunneling model (STM), which assumes that glasses contain a large number of low-energy excitations.^{1,2} These can be viewed as microscopic tunneling systems (TS's) described as double-well potentials (DWP's) in the high-dimensional configuration space of the glass. The Hamiltonian for dielectric glasses, in which we are mainly interested, can be written generally as

$$\mathcal{H} = \mathcal{H}_S + \mathcal{W} + \mathcal{H}_B. \quad (1)$$

\mathcal{H}_S describes the TS's, \mathcal{H}_B the phonon bath, and \mathcal{W} the interaction between TS's and phonons. Whereas the contribution to the specific heat due to TS's only depends on \mathcal{H}_S , contributions to other physical properties like the thermal conductivity, the absorption, or the velocity shift also depend on the interaction between TS's and phonons.³ Therefore, it is of principal interest to specify \mathcal{W} as exactly as possible.

For low temperatures \mathcal{H}_S can be projected on the lowest two eigenfunctions of the TS's. In the localized representation we can write \mathcal{H}_S as a sum of independent TS Hamiltonians h_S , where

$$h_S = \frac{\Delta}{2} \sigma_z + \frac{\Delta_0}{2} \sigma_x, \quad (2)$$

$\sigma_{z,x}$ denoting Pauli matrices. In this representation, σ_z corresponds to the position operator and describes whether the system is on the right ($\sigma_z=1$) or on the left ($\sigma_z=-1$) side of the DWP. Δ denotes the asymmetry and Δ_0 the tunneling matrix element of the corresponding DWP. The energy difference E between the two levels is given by $E = (\Delta^2 + \Delta_0^2)^{1/2}$. Within the STM the distribution of TS's is given by

$$P(\Delta, \Delta_0) = n_{\text{eff}} / \Delta_0. \quad (3)$$

This distribution function corresponds to the least biased choice.

On the basis of elasticity theory \mathcal{W} is normally written as a sum of individual TS-strain interactions w , where

$$w = \gamma e \sigma_z. \quad (4)$$

e denotes the strain field of the glass and γ the deformation potential. The value of γ is a measure for the coupling strength between the TS's and the phonon bath. It turns out that the value of γ depends on the polarization of the strain field.³ Hence we have to distinguish between γ_l and γ_t . Within the STM it is assumed that $\gamma_{l,t}$ are constant values and do not depend on parameters which characterize the TS or the strain field.

Recently we presented a systematic way of finding large numbers of DWP's in structural model glasses.⁴ We chose a simple model glass in which atoms interact via pair potentials. The particular example chosen was NiP (80% Ni, 20% P). On the basis of this set of DWP's we were able to estimate their underlying distribution function in dependence of the potential height, the asymmetry and the distance d between their two minima. The STM is extended by taking the distribution in d into account. Whereas in the previous work we confined ourselves to the microscopic description of \mathcal{H}_S , we now extend our analysis to the interaction \mathcal{W} . To our knowledge, no microscopic estimation of $\gamma_{l,t}$ has been made as yet; however, rough estimations of the deformation potential can be found in Refs. 5 and 6.

The paper is organized as follows. In Sec. II we estimate the velocity of sound $v_{l,t}$. In Sec. III we calculate the deformation potential $\gamma_{l,t}$ based only on statistical assumptions about the nature of the TS's. In Sec. IV we improve our calculation by taking into account the structure of the TS's that we actually found by the above method. It turns out that this improved calculation gives

markedly different results for $\gamma_{l,t}$. Clarifying the reason for this deviation leads to additional insight in the nature of TS's. We confirm (see, e.g., Ref. 7) that the deformation potential is proportional to d . We show that this property results in a dependence of the deformation potential on the energy of the sound waves.

In Sec. V we discuss two major consequences of our analysis. The first point concerns the temperature dependence of the specific heat $C(T)$ and the thermal conductivity $\kappa(T)$. Experimentally it turns out that $C(T) \propto T^{1+\alpha}$ and $\kappa(T) \propto T^{2-\beta}$ with $0.1 \leq \alpha \leq 0.3$ and $0.05 \leq \beta \leq 0.2$.³ In general, one observes $\alpha > \beta$.⁸ It has been stressed that the value of α depends on the time τ_{exp} during which the experiments are performed.⁹ For $\tau_{\text{exp}} = \infty$ the STM predicts $\alpha = 0$, otherwise α is positive. For the value of β the STM predicts $\beta = 0$. The systematic experimental deviations from this prediction prompted several authors to introduce phenomenological distribution functions for TS's in order to explain the experimental results (see, e.g., Ref. 8 and references therein).

In contrast to the STM, our distribution of DWP's yields, even in the limit $\tau_{\text{exp}} = \infty$, a superlinear behavior of $C(T)$.⁴ In this work we will show that $\beta > 0$ also. We will argue that for the correct calculation of β it is essential to take into account the energy dependence of $\gamma_{l,t}$. Only then can the experimental relation $\alpha > \beta$ be obtained.

In a number of recent publications it has been postulated that the phonon-mediated interaction between TS's is much larger than the intrinsic energies connected with TS's (Refs. 10–14). This statement is equivalent to

$$2\pi^2 C_{l,t} \equiv 2\pi^2 \frac{n_{\text{eff}} \gamma_{l,t}^2}{\rho v_{l,t}^2} \geq 1, \quad (5)$$

where ρ is the density of the glass.¹⁰ However, a typical experimental value of $2\pi^2 C_{l,t}$ is $\frac{1}{150}$ (Ref. 15) which would imply that the coupling between TS's is weak. Yu and Leggett have stressed that the experimental results are no final proof that the weak-coupling picture really holds,¹⁰ since the experiments are always analyzed in the framework of the STM which implicitly assumes a weak-coupling between TS's. Therefore, the experimental result $2\pi^2 C_{l,t} \ll 1$ only shows the self-consistence of the theory but does not give a definite answer about the true coupling strength as realized by nature. Hence the true values of n_{eff} and $\gamma_{l,t}$ may be different from the ones determined from experiments. One possible method to decide which picture holds is to estimate n_{eff} and $\gamma_{l,t}$ on a microscopic basis without involving experimental results. In our work⁴ we were able to estimate n_{eff} for NiP, obtaining $n_{\text{eff}} \approx 1.6 \times 10^{46} \text{ J}^{-1} \text{ m}^{-3}$. Therefore, an estimation of $\gamma_{l,t}$ allows us to calculate the value of $2\pi^2 C_{l,t}$. We will confirm the weak-coupling picture supporting the present interpretation of the experimental data. Due to the observed universality of glasses this result might also apply, at least qualitatively, to other glasses.

For reasons of simplicity we always consider a monoatomic model glass. Only for the concrete evaluation of some final results we take into account that NiP contains two different species.

II. ESTIMATION OF THE VELOCITY OF SOUND

Let our model glass consist of N atoms. Its potential energy is given by

$$V_0 = \sum_{i < j} f(r_{ij}), \quad (6)$$

where $r_{ij} \equiv |\mathbf{r}_{ij}| \equiv |\mathbf{r}_i - \mathbf{r}_j|$ describes the distance between atoms i and j . For our simulations we specify $f(r)$ to be

$$f(r) = A[(ar)^{-12} - 1] \exp[1/(ar - c)], \quad ar < c \\ = 0, \quad ar \geq c. \quad (7)$$

This function has been extensively used in the work of Stillinger and Weber.^{16–18} $f(r)$ is an approximation to a Lennard-Jones (LJ) potential. Therefore, we denote our model glass as a *Lennard-Jones-(LJ)-type* glass. Let $\mathbf{r}_{i,0}$ describe the metastable positions of all N atoms in a typical glassy state. For small deviations from this metastable configuration the potential energy may be written approximately as

$$V_0 = \frac{1}{2} \sum_{i < j} f^{(2)}(r_{ij,0}) (r_{ij} - r_{ij,0})^2. \quad (8)$$

$f^{(m)}(r)$ denotes the m th derivative of $f(r)$.

We will calculate the contribution to V_0 from a single sound wave with wave vector \mathbf{q}_σ and polarization vector \mathbf{p} . σ denotes the polarization of the phonon. If we choose $\mathbf{p} \parallel \mathbf{e}_x$, $\mathbf{q}_l \parallel \mathbf{e}_x$, and $\mathbf{q}_t \parallel \mathbf{e}_y$ we may describe a single sound wave (phonon) by

$$\mathbf{r}_i - \mathbf{r}_{i,0} = -i[\exp(iqu_{i,0})b - \exp(-iqu_{i,0})b^*] \frac{1}{\sqrt{N}} \mathbf{e}_x, \quad (9)$$

where $q = |\mathbf{q}_{l,t}|$ denotes the wave number of the wave. In case of a longitudinal wave $u_{i,0}$ is identified with $x_{i,0}$ (the x component of $\mathbf{r}_{i,0}$), in case of a transverse wave it is identified with $y_{i,0}$. b and b^* are proportional to the creation and annihilation operator, respectively. In the limit of long wavelengths q is much smaller than typical nearest-neighbor distances. It follows that

$$\mathbf{r}_{ij} - \mathbf{r}_{ij,0} = u_{ij,0} q \mathcal{Q} \frac{1}{\sqrt{N}} \mathbf{e}_x, \quad (10)$$

where we have identified

$$[\exp(iqu_{i,0})b + \exp(-iqu_{i,0})b^*]$$

with the position operator \mathcal{Q} of the corresponding phonon. For small displacements we obtain from Eq. (10)

$$r_{ij} \approx r_{ij,0} + \frac{u_{ij,0} x_{ij,0}}{r_{ij,0}} q \mathcal{Q} \frac{1}{\sqrt{N}}. \quad (11)$$

Equation (11) is the basis of a coordinate transformation to normal mode coordinates. After the transformation the potential energy reads

$$V_0 = \frac{1}{2N} q^2 \mathcal{Q}^2 \sum_{i < j} f^{(2)}(r_{ij,0}) \frac{(x_{ij,0} u_{ij,0})^2}{r_{ij,0}^2}. \quad (12)$$

In contrast to crystals, in which the influence of a phonon strongly depends on the direction of its wave vector, there is no such dependence for amorphous compounds due to the lack of any long-range order. Therefore, in a first step, we may average over the different directions of the wave vector and the polarization vector. Denoting this average by $\langle \rangle$ we obtain

$$\langle V_0 \rangle = \frac{s_\sigma}{2N} q^2 Q^2 \sum_{i < j} f^{(2)}(r_{ij,0}) r_{ij,0}^2. \quad (13)$$

We have defined $s_l \equiv \langle \hat{y}^4 \rangle$ and $s_t \equiv \langle \hat{x}^2 \hat{y}^2 \rangle$ as averages over the unit sphere. It turns out that $s_l = 1/5$ and $s_t = s_l/3$.

In a second step we take into account the structure of the LJ-type glass. Let us assume that each atom is on average surrounded by n nearest neighbors with distance a , where a is defined by $f^{(1)}(a) = 0$. For rare-gas glasses or metallic glasses like NiP, which are close packed, the coordination number is $n = 12$. The contribution of terms corresponding to pairs which are not nearest neighbors is rather small because $f^{(2)}(r)$ strongly decreases for larger values of r . Therefore, we finally obtain

$$\langle V_0 \rangle \approx \frac{ns_\sigma}{4} f^{(2)}(a) a^2 q^2 Q^2. \quad (14)$$

Identifying $\langle V_0 \rangle$ with $m\omega^2 Q^2/2$, where m describes the mass of the atoms and ω the frequency of the wave, we obtain

$$mv_\sigma^2 \approx \frac{ns_\sigma}{2} f^{(2)}(a) a^2. \quad (15)$$

A direct evaluation of Eq. (13) on the basis of our generated glass configurations yields on average 0.95 times the right side of Eq. (15). Hence our approximation was very reasonable.

We can rewrite Eq. (15) in terms of the average phonon velocity \bar{v} which is defined via $(3\bar{v}^{-3} = 2v_l^{-3} + v_t^{-3})$. Incorporating the numerical factor of 0.95 we finally obtain to a very good approximation

$$m\bar{v}^2 = \frac{2n}{51} f^{(2)}(a) a^2. \quad (16)$$

For the case of a two-component LJ-type glass we simply have to average $f^{(2)}(a) a^2$ over the three different pairs of atoms with the correct statistics. m is now an average mass. For the parameters of NiP, given in Refs. 4 and 18, we have $f^{(2)}(a) a^2 \approx 91\,000$ K and $m \approx 56m_p$. Inserting these values in Eq. (15) we obtain $v_l = 3940$ ms⁻¹, $v_t = 2280$ ms⁻¹, and $\bar{v} = 2530$ ms⁻¹ which compare very well with the experimental values of 5200 ms⁻¹, 2300 ms⁻¹, and 2600 ms⁻¹, respectively.²²⁻²⁴ We have to keep in mind that the original choice of the energy scales in the simulation was determined by the melting temperatures of the pure Ni and P crystals. Furthermore, our analysis shows $v_l^2/v_t^2 = s_l/s_t = 3$. Most experimental values range between 2.3 and 4.0 with an average of 3.2.¹⁵ We are not aware of any physical reason why the experimental ratio for NiP of 5.1 is so large.

III. ANALYTICAL ESTIMATION OF THE DEFORMATION POTENTIAL

In this section we estimate the deformation potential for a "typical" TS, which has to be defined later on. The positions of the atoms for both minima are described by $\mathbf{r}_{i,L}$ and $\mathbf{r}_{i,R}$, respectively. With the definition $\mathbf{d}_i \equiv \mathbf{r}_i^R - \mathbf{r}_i^L$ we can relate the d_i to the total distance d between the two energy minima via $\sum d_i^2 = d^2$.

As a starting point we rewrite the total Hamiltonian as

$$\mathcal{H} = \frac{\Delta_0}{2} \sigma_x + \frac{\mathcal{H}_R - \mathcal{H}_L}{2} \sigma_z + \frac{\mathcal{H}_R + \mathcal{H}_L}{2}. \quad (17)$$

We have explicitly incorporated that the glass may switch between two metastable positions. The tunneling matrix element Δ_0 is a measure for the transition probability amplitude. $\mathcal{H}_{L,R}$ denotes the Hamiltonian of the glass in the neighborhood of the left and of the right energy minimum, respectively. It is obvious that the third term describes the phonon bath and can be identified with \mathcal{H}_B . To a good approximation the corresponding low-frequency phonon displacements are given in analogy to Eq. (9), if the $\mathbf{r}_{i,0}$ are identified with the intermediate structure of the TS, defined by $\mathbf{r}_{i,0} \equiv (\mathbf{r}_{i,R} + \mathbf{r}_{i,L})/2$.

Introducing the strain field via $e = qQ/\sqrt{N}$, it follows from Eq. (11) that

$$\frac{\partial r_{ij}}{\partial e} = \frac{u_{ij,0} \mathbf{x}_{ij,0}}{r_{ij,0}}. \quad (18)$$

Using the relation [see Eq. (4)]

$$\gamma_\sigma = \frac{1}{2} \frac{\partial [\mathcal{H}_R - \mathcal{H}_L]}{\partial e} \quad (19)$$

we obtain

$$\begin{aligned} \gamma_\sigma &= \frac{1}{2} \sum_{i < j} \frac{\partial [f(r)|_{r=r_{ij,R}} - f(r)|_{r=r_{ij,L}}]}{\partial e} \\ &= \frac{1}{2} \sum_{i < j} \frac{u_{ij,0} \mathbf{x}_{ij,0}}{r_{ij,0}} [f^{(1)}(r_{ij,R}) - f^{(1)}(r_{ij,L})]. \end{aligned} \quad (20)$$

It has been experimentally derived from pressure-dependent experiments^{9,25} that even under pressure the number of nearly symmetric DWPs hardly changes. This statement is equivalent to the fact that the deformation potential is not correlated significantly with the asymmetry Δ . Formally this means that the right side of Eq. (20) should be uncorrelated to

$$\sum_{i < j} [f(r_{ij,R}) - f(r_{ij,L})].$$

Taking into account that for $r_{ij} \approx a$ the derivative $f^{(1)}(r_{ij})$ is uncorrelated to $f(r_{ij})$ this property is not surprising. We conclude that the deformation potential has no preferential sign so that we may restrict ourselves to the estimation of γ_σ^2 .

For calculating γ_σ^2 it is necessary to characterize the structure of the glass. As a first try one may assume that the intermediate structure corresponds to the regular closed-packed structure. Using the approximation

$$[f^{(1)}(r_{ij,R}) - f^{(1)}(r_{ij,L})] \approx f^{(2)}(r_{ij,0}) \frac{\mathbf{d}_{ij} \cdot \mathbf{r}_{ij,0}}{r_{ij,0}}, \quad (21)$$

we may write

$$\gamma_\sigma^2 = \frac{1}{16} \left[\sum_i \mathbf{d}_i \cdot \sum_j \frac{u_{ij,0} \mathbf{x}_{ij,0}}{r_{ij,0}^2} f^{(2)}(r_{ij,0}) \mathbf{r}_{ij,0} - \sum_j \mathbf{d}_j \cdot \sum_i \frac{u_{ij,0} \mathbf{x}_{ij,0}}{r_{ij,0}^2} f^{(2)}(r_{ij,0}) \mathbf{r}_{ij,0} \right]^2. \quad (22)$$

Due to the inversion symmetry of the regular closed-packed structure around each atom it is easy to see that both inner sums and hence γ_σ^2 vanish identically. Therefore, some disorder is necessary to obtain a nonzero deformation potential. In this context disorder denotes deviation of the intermediate structure from icosahedral symmetry. We note in passing that consideration of higher-order terms in Eq. (21) gives nonvanishing but small contributions to Eq. (22).

The opposite approach is to assume that the $n=12$ neighbors of a randomly selected atom are distributed arbitrarily around this atom with distance a . Before actually using this model we may, in analogy to above, first perform a spatial average over the directions of the wave and the polarization vectors. The calculation is outlined in the Appendix. We obtain

$$\langle \gamma_\sigma^2 \rangle = \frac{s_\sigma}{4} \sum_{i < j} \sum_{k < l} A_{ijkl,\sigma}, \quad (23)$$

with

$$A_{ijkl,l} = \frac{1}{3} \left[r_{ij,0} r_{kl,0} + 2 \frac{(\mathbf{r}_{ij,0} \cdot \mathbf{r}_{kl,0})^2}{r_{ij,0} r_{kl,0}} \right] \times [f^{(1)}(r_{ij,R}) - f^{(1)}(r_{ij,L})] \times [f^{(1)}(r_{kl,R}) - f^{(1)}(r_{kl,L})] \quad (24)$$

and

$$A_{ijkl,t} = \frac{1}{2} \left[-r_{ij,0} r_{kl,0} + 3 \frac{(\mathbf{r}_{ij,0} \cdot \mathbf{r}_{kl,0})^2}{r_{ij,0} r_{kl,0}} \right] \times [f^{(1)}(r_{ij,R}) - f^{(1)}(r_{ij,L})] \times [f^{(1)}(r_{kl,R}) - f^{(1)}(r_{kl,L})]. \quad (25)$$

It is important to mention that this spatial average does not limit the generality of our approach (in contrast to the assumption about the structure of TS's). Therefore, Eqs. (23)–(25) are still general results.

For calculating the deformation potential for the above model we assume that the individual atoms move independently of each other, i.e., \mathbf{d}_i and \mathbf{d}_j are uncorrelated, and that the relative motion of two atoms during the tunneling process is uncorrelated to their relative position, i.e., \mathbf{d}_{ij} and $\mathbf{r}_{ij,0}$ are uncorrelated. Due to our model, $\mathbf{r}_{ij,0}$ and $\mathbf{r}_{kl,0}$ are also uncorrelated. We indicate the corresponding spatial averages by a second pair of brackets. Performing the statistical averages in Eq. (23) and using the approximation in Eq. (21) it turns out that only terms with $(i,j)=(k,l)$ contribute. After a short calculation

we obtain

$$\begin{aligned} \langle \langle \gamma_\sigma^2 \rangle \rangle &= \frac{s_\sigma}{12} \sum_{i < j} [f^{(2)}(r_{ij,0})]^2 r_{ij,0}^2 (d_i^2 + d_j^2) \\ &\approx \frac{ns_\sigma}{12} [f^{(2)}(a)]^2 a^2 d^2 \\ &\equiv \left[\Gamma_{\sigma,\text{stat}} \frac{d}{a} \right]^2. \end{aligned} \quad (26)$$

In analogy to the previous section we only sum over nearest neighbors. This relation is the main result of the analytical part of this paper. The deformation potential varies for different TS's because of its dependence on d . The consequences will be discussed later on. For the case of NiP it turns out $\Gamma_{l,\text{stat}} = 3.51$ eV and $\Gamma_{t,\text{stat}} = \Gamma_{l,\text{stat}}/\sqrt{3}$.

IV. COMPUTATIONAL ESTIMATION OF THE DEFORMATION POTENTIAL

A priori it is not clear how far the above assumptions hold. For example, we have neglected the condition that the n atoms which surround one randomly selected atom must have a minimum distance between each other. This condition could be incorporated in an improved statistical analysis. Since the intermediate structure approaches icosahedral symmetry we would expect a decrease of $\langle \langle \gamma_\sigma^2 \rangle \rangle$ as compared to Eq. (26).

For the related case of low-frequency localized vibrations in glasses Schober and Laird could show that the nearest-neighbor shell of the central atom of such a mode is less dense than the average nearest-neighbor shell.^{19,20} This interesting result suggests that TS's tend to occur in nontypical regions of the glass, so that a statistical analysis of TS's, based on typical regions, might give misleading results. Therefore, rather than refining our statistical analysis, we try to calculate the deformation potential via Eq. (23) exactly for the DWP's which we found by our numerical method (see the Introduction). Our analysis will be based on 71 DWP's. For notational simplicity we will omit the brackets when referring to γ_σ . The values for $[\gamma_l/(d/a)]^2$ for all 71 DWPs are shown in Fig. 1 as a function of d/a . Despite large fluctuations, $[\gamma_l/(d/a)]^2$ is largely independent of (d/a) , in agreement with the results of the previous section. A least-square fit yields $\gamma_l = \Gamma_l(d/a)$ with $\Gamma_l = 1.07$ eV. Surprisingly, Γ_l differs markedly from our above estimation $\Gamma_{l,\text{stat}}$. Since we have a microscopic description of the TS's, it is possible to check at which point the assumptions which lead to the calculation of $\Gamma_{l,\text{stat}}$ are in error. For this purpose we introduce χ_i ($i=1, \dots, 5$) via

$$\chi_1 = \sum'_{i < j} d_{ij}^2 / nd^2, \quad (27)$$

$$\chi_2 = \sum'_{i < j} \frac{(\mathbf{d}_{ij} \cdot \mathbf{r}_{ij,0})^2}{r_{ij,0}^2} / \sum'_{i < j} \frac{d_{ij}^2}{3}, \quad (28)$$

$$\chi_3 = \sum'_{i < j} (r_{ij,L} - r_{ij,R})^2 / \sum'_{i < j} \frac{(\mathbf{d}_{ij} \cdot \mathbf{r}_{ij,0})^2}{r_{ij,0}^2}, \quad (29)$$

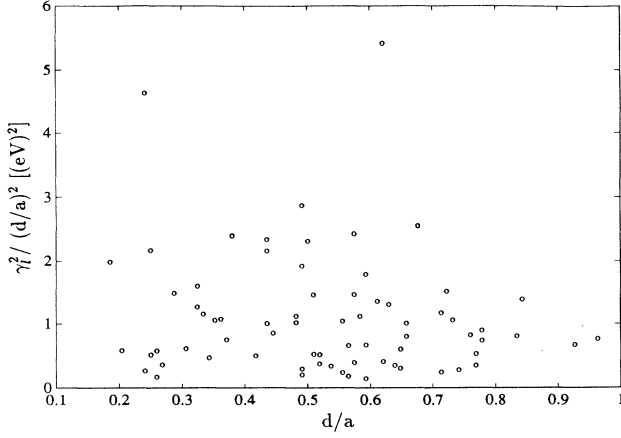


FIG. 1. The dependence of $\gamma_l^2/(d/a)^2$ on (d/a) for 71 analyzed DWP's for the case of NiP.

$$\chi_4 = \sum_{i < j} A_{ijij,\sigma} / \sum'_{i < j} [f_{ij}^{(2)}(a_{ij})]^2 a_{ij}^2 (r_{ij,L} - r_{ij,R})^2, \quad (30)$$

$$\chi_{5,\sigma} = \sum_{i < j} \sum_{k < l} A_{ijkl,\sigma} / \sum_{i < j} A_{ijij,\sigma}. \quad (31)$$

The prime indicates that the sum only extends over nearest neighbors. We introduced additional indices for $f_{ij}^{(2)}$ and a_{ij} because for this analysis we explicitly have to take into account that NiP consists of two species described by three different equilibrium distances and three differential potential functions. We use the convention that two atoms are nearest neighbors if their average distance is less than $1.2 a_{ij}$. We have defined the χ_i such that on average

$$\Gamma_\sigma^2 \approx \chi_1 \chi_2 \chi_3 \chi_4 \chi_{5,\sigma} \Gamma_{\sigma,\text{stat}}^2.$$

If all statistical assumptions were fulfilled, we would obtain $\chi_1 = \chi_2 = \chi_3 = \chi_4 = 1$. As already mentioned $\chi_{5,\sigma}$ is a measure for the disorder of the glass. In case of pure disorder, as defined in the previous section, we have $\chi_{5,\sigma} = 1$, whereas complete icosahedral symmetry of the intermediate structure gives $\chi_{5,\sigma} = 0$.

On the basis of our 71 DWP's we obtain the following average values for the χ_i : $\chi_1 = 0.70$, $\chi_2 = 0.39$, $\chi_3 = 0.99$, $\chi_4 = 0.47$, $\chi_{5,l} = 0.69$, $\chi_{5,t} = 0.86$. The rather small value of χ_2 indicates strong correlations between $\mathbf{r}_{ij,0}$ and \mathbf{d}_{ij} . It means that two nearest neighbors favor a relative movement perpendicular to the vector which connects both atoms. In this way the change in distance is as small as possible which is very favorable energetically. $\chi_4 \ll 1$ can be explained as follows: the sum on the right side of Eq. (23) is dominated by terms with large values of $|r_{ij,L} - r_{ij,R}|$. For energetic reasons the distance between two atoms cannot be much smaller than a . Therefore, in general, a large change in distance can only be accomplished if $r_{ij,L}$ or $r_{ij,R}$ is significantly larger than a . It is then no longer justified to evaluate $f^{(2)}$ at the point $r = a$ but one has to choose $r = r_0$ with $r_0 > a$. As the second derivative of $f(r)$ strongly decreases with increasing r it is obvious that the terms which should contribute most

are strongly reduced. As already predicted $\chi_{5,\sigma}$ is also smaller than 1 but we see that our original statistical description of the "typical" TS, yielding $\chi_{5,\sigma} = 1$, was reasonable.

Γ_t can be calculated in analogy to Γ_l . We obtain $\Gamma_t^2/\Gamma_l^2 = 2.35$. The typical experimental value is 2.5.¹⁵ We see that our calculation, based on computer generated TS's, yields a more realistic value for this ratio than the value of 3 which was the result of our statistical analysis.

Combining the results of the previous sections we may finally write to a good approximation

$$\Gamma_l = \frac{m\bar{v}^2}{\sqrt{n}} \quad (32)$$

and

$$\Gamma_t = \frac{2m\bar{v}^2}{3\sqrt{n}}, \quad (33)$$

showing that the coupling between TS's and phonons can be calculated from just the knowledge of m , \bar{v} , and n .

V. DISCUSSION

First we discuss some implications of our results for the temperature dependencies of $\kappa(T)$ and the relation between α and β . In this context we will show how to estimate γ_σ for a specific compound like NiP.

The densities of TS's which are relevant for the thermal conductivity and the specific heat can be calculated from the distribution of DWP's via

$$n_{\text{eff}}(E) = \left\langle \frac{\Delta_0^2}{E^2} \delta(E - \sqrt{\Delta^2 + \Delta_0^2}) \right\rangle \quad (34)$$

and

$$n_{\text{total}}(E, \tau_{\text{exp}}) = \langle \delta(E - \sqrt{\Delta^2 + \Delta_0^2}) \Theta(\tau_{\text{exp}} - \tau_{\text{rel}}) \rangle, \quad (35)$$

respectively, where the brackets denote an average over the distribution of DWP's. τ_{rel} denotes the relaxation time of a TS in a phonon bath which is given by

$$\tau_{\text{rel}}^{-1} = \left[\frac{2\gamma_t^2}{v_t^5} + \frac{\gamma_l^2}{v_l^5} \right] \frac{E\Delta_0^2}{2\pi\rho\hbar^4} \coth(E/2k_B T). \quad (36)$$

Because of the step function on the right side of Eq. (35), $n_{\text{total}}(E, \tau_{\text{exp}})$ only takes into account TS's with relaxation times smaller than τ_{exp} .

The deformation potential may be experimentally determined via acoustic attenuation measurements.¹⁵ For example, the inverse mean free path of a phonon with energy E , interacting resonantly with TS's, is given by

$$\begin{aligned} l_\sigma^{-1} &= \frac{\pi E \tanh(E/2k_B T)}{\hbar\rho v_t^3} \left\langle \delta(E - \sqrt{\Delta^2 + \Delta_0^2}) \frac{\Delta_0^2}{E^2} \Gamma_\sigma^2 \frac{d^2}{a^2} \right\rangle \\ &\equiv \frac{\pi E \tanh(E/2k_B T)}{\hbar\rho v_t^3} \gamma_\sigma^2 n_{\text{eff}}(E), \end{aligned} \quad (37)$$

with

$$\gamma_\sigma^2 \equiv \Gamma_\sigma^2 \frac{d_{\text{eff}}^2(E)}{a^2} \quad (38)$$

and

$$d_{\text{eff}}^2(E) \equiv \frac{\langle \delta(E - \sqrt{\Delta^2 + \Delta_0^2})(\Delta_0^2/E^2)d^2 \rangle}{n_{\text{eff}}(E)}. \quad (39)$$

We have written Eq. (37) in this unusual form to emphasize that it is not justified *a priori* to use a constant value for γ_σ . Numerical evaluation of Eq. (39) yields $d_{\text{eff}}(E) = 0.36a$ if we choose $E/k_B = 1$ K. From this value we determine $\gamma_l = 0.38$ eV and $\gamma_t = 0.25$ eV. We will discuss these values further below.

To obtain the temperature dependence of the specific heat $C(T)$ and the thermal conductivity $\kappa(T)$, we have to know the energy dependencies of

$$n_{\text{total}}(E, \tau_{\text{exp}}) \propto E^{\delta_1(\tau_{\text{exp}})},$$

$n_{\text{eff}}(E) \propto E^{\delta_2}$ and $d_{\text{eff}}^2(E) \propto E^{\delta_3}$. Then α and β are simply given by $\alpha = \delta_1(\tau_{\text{exp}})$ and $\beta = \delta_2 + \delta_3$. For $C(T)$ it is important to specify the experimental time τ_{exp} during which the measurements are performed. We already mentioned that even within the STM for finite τ_{exp} the temperature dependence of $C(T)$ is superlinear. Given the distribution of DWP's it is straightforward to calculate $\delta_1(\tau_{\text{exp}})$, δ_2 , and δ_3 . For the calculation of τ_{exp} of NiP we used the calculated values of γ_σ and v_σ . The density is given by $\rho = 8350 \text{ kg m}^{-3}$. We find $\delta_1(\tau_{\text{exp}} = \infty) = 0.09$ and $\delta_1(\tau_{\text{exp}} = 5 \text{ s}) = 0.29$. $\tau_{\text{exp}} = 5 \text{ s}$ is a typical experimental time for a specific-heat measurement. Furthermore, we obtain $\delta_2 = 0.28$, $\delta_3 = -0.14$ and therefore $\alpha = 0.29$ and $\beta = 0.14$ in excellent agreement with typical experimental values. δ_3 is negative because with decreasing d typical tunneling matrix elements Δ_0 and hence typical energies E become larger. Neglecting the energy dependence of $d_{\text{eff}}(E)$ or, equivalently, of γ_σ , we would obtain a value of β so large that we would not verify the experimental relation $\alpha > \beta$. In order to visualize the effect of the energy dependence of $d_{\text{eff}}(E)$ we have plotted the energy dependence of γ_l in Fig. 2. Although knowledge of the distribution of DWP's is necessary for obtaining the quantitative values we would like to stress that general features like the energy dependence of the deformation potential can qualitatively already be deduced without exact knowledge of this distribution. The important ingredient is only the dependence of $\gamma_{l,t}$ on d/a .

We are now in a position to check the coupling strength between the individual TS's which is expressed by the value of $C_{l,t}$. In Ref. 4 we obtained $n_{\text{eff}} = 1.6 \times 10^{46} \text{ J m}^{-3}$. Together with the experimental values of $v_{l,t}$ and ρ and the calculated values of $\gamma_{l,t}$ we obtain $2\pi^2 C_l = 1/85$ and $2\pi^2 C_t = 1/185$ which is in excellent agreement with the typical experimental value $2\pi^2 C_{l,t} = 1/150$. We conclude that, in accordance with the STM and in contrast to the proposal by Yu and Leggett,¹⁰ the TS's in NiP may be described in the framework of the weak-coupling picture. Due to the observed universality of glasses²¹ it would be surprising if the weak-coupling picture would not hold in other glasses,

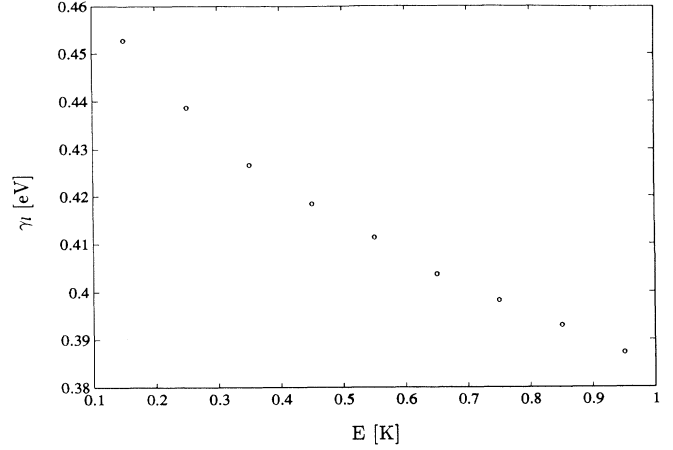


FIG. 2. Energy dependence of γ_l for NiP.

too.

C_t has been experimentally determined for NiP.²²⁻²⁴ From the temperature dependence of the shift of the velocity of sound the authors obtain $2\pi^2 C_t = 1/840$. In contrast, analysis of the thermal conductivity yields $2\pi^2 C_t = 1/120$. For the thermal conductivity it is important to subtract the effect of the electrons; because of the uncertainties of this subtraction the first value is considered to be more trustworthy. Arguments can be found in the literature why the "true" value should lie somewhere in between.^{26,27} Our estimation agrees better with the second value.

In summary, we have presented a microscopic estimation of the deformation potential of LJ-type glasses. We have shown that, on the one hand, the deformation potential is energy dependent which strongly influences the temperature dependence of the thermal conductivity and that, on the other hand, the coupling between TS's is weak so that the STM is sufficient to explain the dynamics of TS's in glasses at very low temperatures.

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APPENDIX

In this appendix we would like to sketch the derivation of Eqs. (24) and (25). We choose $\mathbf{q}_l \parallel \mathbf{u}_1$, $\mathbf{q}_l \parallel \mathbf{u}_2$, and $\mathbf{p} \parallel \mathbf{u}_2$ with $\mathbf{u}_1 \perp \mathbf{u}_2$ and $|\mathbf{u}_1| = |\mathbf{u}_2| = 1$. Furthermore, we define $\mathbf{u}_3 = \mathbf{u}_1 \times \mathbf{u}_2$. For reasons of simplicity we take $\mathbf{r}_{ij} = (1, 0, 0)$ and $\mathbf{r}_{kl} = (\cos\varphi, \sin\varphi, 0)$. We are interested in the expression

$$W_\sigma = \langle (\mathbf{r}_{ij} \cdot \mathbf{q}_\sigma)(\mathbf{r}_{ij} \cdot \mathbf{p})(\mathbf{r}_{kl} \cdot \mathbf{q}_\sigma)(\mathbf{r}_{kl} \cdot \mathbf{p}) \rangle, \quad (A1)$$

where we average over all possible directions of the wave and the polarization vector. Using $\langle u_{1,x}^4 \rangle = 1/5$ and $\langle u_{1,x}^2 u_{1,y}^2 \rangle = 1/15$ we immediately obtain

$$W_l = \frac{1}{15}(1 + 2 \cos^2\varphi). \quad (A2)$$

Now we concentrate on the calculation of W_t . From

$$\left\langle (\mathbf{r}_{ij} \cdot \mathbf{u}_1)^2 \sum_{m=1}^3 (\mathbf{r}_{kl} \cdot \mathbf{u}_m)^2 \right\rangle = \langle (\mathbf{r}_{ij} \cdot \mathbf{u}_1)^2 \rangle = \frac{1}{3} \quad (\text{A3})$$

it follows that

$$\langle (\mathbf{r}_{ij} \cdot \mathbf{u}_1)^2 (\mathbf{r}_{kl} \cdot \mathbf{u}_2)^2 \rangle = \frac{1}{6} - \frac{W_l}{2} = \frac{1}{15} (2 - \cos^2 \varphi) . \quad (\text{A4})$$

Squaring the Lagrange identity

$$(\mathbf{r}_{ij} \cdot \mathbf{u}_1)(\mathbf{r}_{kl} \cdot \mathbf{u}_2) - (\mathbf{r}_{ij} \cdot \mathbf{u}_2)(\mathbf{r}_{kl} \cdot \mathbf{u}_1) = (\mathbf{r}_{ij} \times \mathbf{r}_{kl})(\mathbf{u}_1 \times \mathbf{u}_2)$$

(A5)

on both sides it turns out

$$W_t = \frac{1}{2} \langle (\mathbf{r}_{ij} \cdot \mathbf{u}_1)^2 (\mathbf{r}_{kl} \cdot \mathbf{u}_2)^2 + (\mathbf{r}_{ij} \cdot \mathbf{u}_2)^2 (\mathbf{r}_{kl} \cdot \mathbf{u}_1)^2 \rangle$$

$$- \frac{1}{2} \langle [(\mathbf{r}_{ij} \times \mathbf{r}_{kl})(\mathbf{u}_1 \times \mathbf{u}_2)]^2 \rangle$$

$$= \frac{1}{15} (2 - \cos^2 \varphi) - \frac{1}{6} \sin^2 \varphi = \frac{1}{30} (3 \cos^2 \varphi - 1) . \quad (\text{A6})$$

Equations (24) and (25) are hence justified.

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